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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/542,789	07/20/2005	Israel Rubinstein	RUBINSTEIN9A	2392
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EXAMINER				
HORNING, JOEL G				
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Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Office Action Summary

Application No.

10/542,789

Applicant(s)

RUBINSTEIN ET AL.

Examiner

JOEL G. HORNING

Art Unit

1792

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --
Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

- 1) ☒ Responsive to communication(s) filed on 24 December 2008.
- 2a) ☒ This action is **FINAL**. 2b) ☐ This action is non-final.
- 3) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

- 4) ☒ Claim(s) 1-15, 17-23, 25-27, 32 and 33 is/are pending in the application.
- 4a) Of the above claim(s) 24 and 28-31 is/are withdrawn from consideration.
- 5) ☐ Claim(s) _____ is/are allowed.
- 6) ☒ Claim(s) 1-15, 17-23, 25-27, 32 and 33 is/are rejected.
- 7) ☐ Claim(s) _____ is/are objected to.
- 8) ☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

- 9) ☐ The specification is objected to by the Examiner.
- 10) ☐ The drawing(s) filed on _____ is/are: a) ☐ accepted or b) ☐ objected to by the Examiner.
Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).
Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).
- 11) ☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

- 12) ☒ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
- a) ☒ All b) ☐ Some * c) ☐ None of:
1. ☒ Certified copies of the priority documents have been received.
 2. ☐ Certified copies of the priority documents have been received in Application No. _____.
 3. ☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

- 1) ☒ Notice of References Cited (PTO-892)
- 2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
- 3) ☐ Information Disclosure Statement(s) (PTO/SB/08)
Paper No(s)/Mail Date _____
- 4) ☐ Interview Summary (PTO-413)
Paper No(s)/Mail Date _____
- 5) ☐ Notice of Informal Patent Application
- 6) ☐ Other: _____

DETAILED ACTION

Election/Restrictions

This application contains claims 24 and 28-31 drawn to an invention nonelected with traverse in the reply filed on 06-19-2008. A complete reply to the final rejection must include cancellation of nonelected claims or other appropriate action (37 CFR 1.144) See MPEP § 821.01.

Claim Rejections - 35 USC § 102

(b) the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of application for patent in the United States.

Claims 1-4, 7, 8, 25, 32 and 33 are rejected under 35 U.S.C. 102(b) as being anticipated by Kovtyukhova et al (Materials Science and Engineering C 19 (2002) 255-262).

1. The instant claim 1 requires a method of preparing a material composed of nanoparticles comprising:
 - a. Providing a substrate having pores or channels functionalized with an agent capable of binding nanoparticles, with said pores or channels having a desired shape and a cross-sectional size from several nanometers to several hundreds of microns;
 - b. Passing through said substrate a colloid solution comprising nanoparticles and a solvent, so as to bind and form more than one layer of nanoparticles in the pores or channels, where the nanoparticles spontaneously coalesce to form a coherent material;

- c. Thereby obtaining in said pores or channels a material composed of nanoparticles having a hollow structure that follows the shape of the pores or channels in the substrate.
2. The instant independent claim 25 is a product-by-process claim that could be produced by the process of claim 1. Since it is a product claim, only the structure that would result from the process is given patentable weight. It requires that the material be composed of more than one layer of nanoparticles that have coalesced as a coherent material, with a hollow structure, either in the shape of a pore or a channel.

Kovtyukhova et al teach a process of forming a material composed of (including) nanoparticles which involves providing a membrane with pores where the surface of the pores has been functionalized with an agent (PEI). The membranes are composed of alumina (**claims 7 and 8**) with pores of the desired tubular shape 200nm (**claim 3**). They teach using a layer-by-layer deposition process wherein a solution of metal oxide nanoparticles (**claim 4**) and a solvent is passed through the membrane, followed by a polymer solution and repeated until a multilayer structure composed of the nanoparticles is produced. Since the layers are connected, they are coherent. Since the connection of the layers occurs when the solutions are passed through the membrane, the coalescence of the nanoparticles is spontaneous. This results in a multilayer structure of nanoparticles in the pores having a hollow structure that follows the shape of the pores (**claims 1, 16 and 25**) (section 2.2 (1) and figure 2). It is clearly envisaged from figure 2 that Kovtyukhova et al also teach using alumina membranes where the nanopores penetrate from one side of the substrate to the other side (**claim**

32). They further teach dissolving the membrane to separate the nanotubes from the membrane (**claims 2 and 33**) (figure 2 [a-d]).

Claim Rejections - 35 USC § 103

The factual inquiries set forth in *Graham v. John Deere Co.*, 383 U.S. 1, 148 USPQ 459 (1966), that are applied for establishing a background for determining obviousness under 35 U.S.C. 103(a) are summarized as follows:

1. Determining the scope and contents of the prior art.
2. Ascertaining the differences between the prior art and the claims at issue.
3. Resolving the level of ordinary skill in the pertinent art.
4. Considering objective evidence present in the application indicating obviousness or nonobviousness.

This application currently names joint inventors. In considering patentability of the claims under 35 U.S.C. 103(a), the examiner presumes that the subject matter of the various claims was commonly owned at the time any inventions covered therein were made absent any evidence to the contrary. Applicant is advised of the obligation under 37 CFR 1.56 to point out the inventor and invention dates of each claim that was not commonly owned at the time a later invention was made in order for the examiner to consider the applicability of 35 U.S.C. 103(c) and potential 35 U.S.C. 102(e), (f) or (g) prior art under 35 U.S.C. 103(a).

3. Claims 5, 6, 9-11, 17, 20, 26 and 27 are rejected under 35 U.S.C. 103(a) as being unpatentable over Kovtyukhova et al (Materials Science and Engineering C 19 (2002) 255-262) in view of Liu et al (Chemical Physics Letters 298 (1998) 315-319) in view of Braunstein et al (Chem. Eur. J. 2000, 6, No24, pages 4637-4646).

4. The instant **claim 20** is directed toward a method for forming gold nanotubes comprising:

- a. Providing a substrate having nanopores functionalized with an agent capable of binding gold nanoparticles, said nanopores penetrating from one side of the substrate to the other side and having a diameter of about 20nm to 500nm;
- b. Passing through said substrate a colloid solution comprising stabilized gold nanoparticles and water, so as to bind and form in the nanopores more than one layer of gold nanoparticles, where the nanoparticles spontaneously coalesce to form coherent nanotubes comprising gold;
- c. Optionally, separating the gold nanotubes from the substrate.

Claim 5 (dependent upon claim 4) further requires that the material be a metal based material.

Claim 6 (dependent upon claim 5) further *optionally* requires that the metal nanoparticle based material be separated from the substrate.

Kovtyukhova et al teach a process of forming a material composed of (including) nanoparticles which involves providing a membrane with pores where the surface of the pores have been functionalized with an agent (PEI). The membranes are composed of alumina with pores of the desired tubular shape 200nm. They teach using a layer-by-layer deposition process wherein a solution of metal oxide nanoparticles and a solvent is passed through the membrane, followed by a polymer solution and repeated until a multilayer structure composed of the nanoparticles is produced. Since the layers are connected, they are coherent. Since the connection of the layers occurs when the

solutions are passed through the membrane, the coalescence of the nanoparticles is spontaneous. This results in a multilayer structure of nanoparticles in the pores having a hollow structure that follows the shape of the pores (section 2.2 (1) and figure 2). They further teach dissolving the membrane to separate the nanotubes from the membrane (figure 2 [a-d]).

As is readily apparent from figure 2, Kovtyukhova et al also teach using alumina membranes where the nanopores penetrate from one side of the substrate to the other side. They also teach using nanoparticles generally as the base material for a variety of nanoscale electronic components. They teach that "a real challenge in the practical use of these [nanoscale electronic components] is the problem of making the appropriate connections between nanoscale devices..." As discussed above, they also teach depositing multilayers of nanoparticles into the tubular pores of alumina membranes to produce electronic structures, but they do not specifically teach using metal nanoparticles (Introduction).

Liu et al teach using a similar layer-by-layer deposition process in order to form multilayer films of metal nanoparticles for the construction of 3-D highly conductive structures, made specifically of gold (**claims 5, 6 and 10**), onto substrates in such a way that the electrical properties of the multilayer can be controlled for the creation of nanostructured electrical devices. Liu et al teach that it is known to use gold colloidal solutions with nanoparticles with varying diameters, including 11 nm in diameter for such multilayers (**claim 17**) (Introduction, page 315) and that the gold nanoparticles are

stabilized by organic stabilizers (cationic polymer molecules) (**claim 11**, introduction page 316).

Thus it would have been obvious to a person of ordinary skill in the art at the time of invention to substitute the TiO_2 nanoparticle layers in the multilayer deposition of Kovtyukhova et al for the gold nanoparticle multilayers of Liu et al in order to produce a templated nanoparticle structure of gold nanoparticles with tunable conductivities (**claims 5 and 6**). Such a person would be motivated to do so in order to produce connectors between nanoscale devices with tunable conductivities and predictable results.

Kovtyukhova et al teach using PEI on the alumina substrate to bind the alumina membrane with the TiO_2 nanoparticles, however, they do not specify that the PEI is a bifunctional agent.

However, Braunstein et al teach that "the nature of the chemical interactions between the metal clusters or colloids and the nanoporous cavity will play an essential role in determining their organization and confinement inside the pores. It therefore becomes particularly attractive to attempt the functionalization of the interior pore surface to improve the selectivity of these interactions." They teach that in order to bind gold metal nanoparticles to the surface of alumina membranes, bifunctional agents with one moiety that binds to the alumina $-\text{OH}$ terminated surface and another that strongly binds to the metal clusters have been used and successfully immobilize the clusters on the alumina membrane surface (Introduction, page 4638, right column).

Thus, it would have been obvious to a person of ordinary skill in the art at the time of invention to substitute the binding agent on the alumina substrate used by Kovtyukhova et al to bind the alumina with the TiO₂ nanoparticles (PEI) for an appropriate bifunctional agent with a moiety that binds to the alumina and another that binds with the gold nanoparticles: immobilizing the gold nanoparticles and improving the selectivity of the nanoparticle/membrane wall interaction in order to better control the structure and organization of the resulting gold nanoparticle layers (**claims 9 and 20**).

Claims 26 and 27 depend upon the product-by-process claim 25 and further require that the material be nanotubes about 200nm in diameter composed of gold nanoparticles about 10-20nm in diameter.

As discussed above for claim 17, Kovtyukhova et al in view of Liu et al teach forming nanotubes ~200nm in diameter composed of gold nanoparticles 11nm in diameter. It would have been obvious to a person of ordinary skill in the art at the time of invention to do so for the reasons cited above.

5. **Claims 12-13** are rejected under 35 U.S.C. 103(a) as being unpatentable over Kovtyukhova et al in view of Liu et al in view of Braunstein et al, as applied to claim 11 above, further in view of Mougin et al. (Colloids and Surfaces A: Physicochem. Eng. Aspects 193 (2001) 231-237).

Claims 12-13 are directed towards using tri-sodium citrate dehydrate salt as an organic stabilizer for the nanoparticles.

Kovtyukhova et al in view of Liu et al teach using stabilizers for the gold nanoparticles, but do not teach using tri-sodium citrate dihydrate. However, Mougin et

al teach the stabilization of gold nanoparticles with tri-sodium citrate dihydrate (citric acid trisodium) (Experimental section, page 233).

It would have been obvious to a person of ordinary skill in the art at the time of invention to substitute the polymeric stabilizers of Kovtyukhova et al in view of Liu et al with the known stabilizer tri-sodium citrate dihydrate to perform the same function and produce predictable results.

9. **Claims 14 and 15** are rejected under 35 U.S.C. 103(a) as being unpatentable over Kovtyukhova et al in view of Liu et al and Braunstein et al as applied to claim 9 above, and further in view of Mardilovich et al (**Journal of Membrane Science**, Volume 98, Issues 1-2, 13 January 1995, Pages 143-155).

Claims 14 and 15 require that the alumina membrane be dissolved in an acid or a base.

As discussed above, Kovtyukhova et al in view of Liu et al teach separating the material from the alumina membrane by dissolving the alumina membrane, but do not teach how exactly they do that. However, Mardilovich et al teach that "Conventional (amorphous) AA [anodic alumina] membranes are unique ceramic sieves, however, they have very little resistance to acid and base attack. The dissolution process of amorphous AA membranes begins at pH <5.0 and pH >8.2. If the contact time is long enough (in basic media it may be only some hours), such membranes can be completely dissolved at pH<4.2 and pH>9.9 (in HCl and NaOH)" (conclusions).

Thus it would have been obvious to a person of ordinary skill in the art at the time of invention to dissolve the alumina membrane in either an acid or a base. Such a

person would have been motivated to do so in order to effectively dissolve the alumina membrane.

10. Claims 18, 19, and 21-23 are rejected under 35 U.S.C. 103(a) as being unpatentable over Kovtyukhova et al in view of Liu et al and Braunstein et al as applied to claims 1, 6 and 20 above, and further in view of Martin et al (J. Phys. Chem. B 2001, 105, 1925-1934).

The instant claims are directed towards coating the inside of the nanoparticle multilayer material with a metal layer to form a material that is still hollow.

Kovtyukhova et al in view of Liu et al teach electrolessly plating the inside of the nanotube material with a layer of gold (Kovtyukhova et al 2.2 (1)). However, they do not teach leaving the inside of the nanotube hollow, but rather entirely fill the tube to form gold rods.

Martin et al teaches that "[i]n the electroless method, metal deposition begins at the pore walls creating, at a short deposition time, hollow metal nanotubules within the pores. That is, the electroless plating method yielded metal (typically gold) nanotubule membranes" (introduction page 1925). By controlling the gold deposition time they can control the inside diameter of the nanotube (figure 2). They studied the transport properties of the nanotubes in the membranes and teach that they "might be useful as molecular sieves" (Introduction, page 1925) and that "[b]ecause the nanotubules are composed of an electronically conductive material (Au), it is possible to change the transport properties of these membranes electrochemically" (Section V, page 1931).

Thus it would have been obvious to a person of ordinary skill in the art at the time of invention to decrease the deposition time for the gold electroless deposition in order to produce hollow gold nanotubes (**claims 18, 19, 21 and 23**), such a person would have been motivated to do so in order to produce filters with electrochemical control over the transport properties.

11. **Claim 22** further requires that the metal deposited inside of the nanotube be copper.

Kovtyukhova et al in view of Liu et al in view of Braunstein et al further in view of Martin et al teach the deposition of gold as the conductive layer forming the inside diameter of the sieves.

However, it would have been obvious to a person of ordinary skill in the art to substitute the gold metal coating on the gold nanoparticles for a copper metal coating because they are both well known as conductive materials and so, as taught by Martin above, it would be possible for either one to change the transport properties of the nanotubes electrochemically, with the substitution producing predictable results. Such a person would have been motivated to do so in order to produce a product that is conductive with the same dimensions, but with materials that are less expensive (the examiner takes official notice that it is well known that, by volume, copper is less expensive than gold) and have a product that would as a result be less expensive to produce.

Response to Amendment

12. In response to applicant's amendments of 12-24-2008, examiner's objections to the specification and claim 16 are withdrawn as well as examiner's rejection of claims 1-23, 25-27, 32 and 33 under 35 USC 112 2nd paragraph.

Response to Arguments

13. Applicant's arguments filed 12-24-2008 have been fully considered but they are not persuasive.

14. Applicant's argument "1" is that polyethyleneimine (PEI) is not capable of binding nanoparticles. As demonstrated by polymer chemistry innovations (http://www.polychemistry.com/products_linear_pei.php, retrieved 03-23-2009), PEI is known to the art as an adhesion promoting agent, capable of binding a variety of materials to each other (e.g. polyolefins, metals, etc). Thus it is capable of binding nanoparticles of those materials and meets the claim limitations. It is additionally noted that the claim language does not require that the agent actually be capable of binding the specific nanoparticles of the process, just that it be capable of binding some kind of nanoparticle.

15. Applicant's argument "2" is that immersing a substrate in a solution is different than passing a solution through a substrate. However, passing a solution through a substrate only requires that some material flow from one side of the substrate to the other side during the process. It is readily apparent that during the prior art process, solution will pass from one side of the substrate to the other (e.g. by capillary action when the membrane is added to the bath and the pores are filled with solution, by diffusion during the soaking step in the bath, or even during the washing process when

solvents are forced through the membrane to remove excess film forming material from the pores (forcing film forming material along with the cleaning agent from one side of the membrane and through the other side along)).

16. Applicant's argument "3" is that Kovtyukhova would not spontaneously coalesce to form a coherent material.

Specifically, applicant argues that the Kovtyukhova washing step is evidence that the coalescing is not spontaneous. If the coalescing was not spontaneous, a processing step would need to be performed in order to allow the material to coalesce into the coherent tube structure (e.g. a sintering treatment to melt materials together). Since the washing step would remove material that has not coalesced into the deposited layer, this step actually indicates that the coalescing is spontaneous because if it were not, the washing step would simply remove all of the nanoparticles every time it is performed and Kovtyukhova would not be able to deposit a coating inside the pores.

Applicant then argues that the further deposition of a metal layer inside the nanotubes indicates that the growth is not spontaneous. Examiner does not understand why this would indicate that the growth is not spontaneous, but directs applicant to their own claims 18, 19 and 21-23 where such a further metal deposition process is required for their own nanoparticles which are necessarily spontaneously coalesced into a coherent material.

17. Applicant's argument "4" is that the coating of Kovtyukhova does not conform to the shape of the pores and evidences this by citing Kovtyukhova, page 259, second column, lines 1-5. First, this citation is directed towards a different embodiment of

Kovtyukhova which formed very different striped nanorods (see figure 1) instead of the tubes formed in the embodiment used in the presented rejection (see figure 2). It is readily apparent from figure 2 that in the embodiment used in the rejection the deposited material does follow the shape of the pores.

18. Applicant's argument "5" is that Kovtyukhova would not produce a hollow structure. Examiner directs applicant to the TEM images of hollow tubes formed by the Kovtyukhova process figures 2(a-d).

19. In response to applicant's argument that the references fail to show certain features of applicant's invention, it is noted that the features upon which applicant relies (i.e., "a one step method of producing more than one layer of nanoparticles" or "only one solution is passed through the pores") are not recited in the rejected claim(s). Although the claims are interpreted in light of the specification, limitations from the specification are not read into the claims. See *In re Van Geuns*, 988 F.2d 1181, 26 USPQ2d 1057 (Fed. Cir. 1993).

20. Applicant's argument that Braunstein does not anticipate applicant's claims is not relevant because an 102 rejection of applicant's claims over Braunstein was not made. Braunstein is used in 103 rejection to teach the obviousness of applying *bi-functional* binding agents on the pore surfaces, which applicant has not traversed.

Conclusion

21. **No current claims are allowed.**

THIS ACTION IS MADE FINAL. Applicant is reminded of the extension of time policy as set forth in 37 CFR 1.136(a).

A shortened statutory period for reply to this final action is set to expire THREE MONTHS from the mailing date of this action. In the event a first reply is filed within TWO MONTHS of the mailing date of this final action and the advisory action is not mailed until after the end of the THREE-MONTH shortened statutory period, then the shortened statutory period will expire on the date the advisory action is mailed, and any extension fee pursuant to 37 CFR 1.136(a) will be calculated from the mailing date of the advisory action. In no event, however, will the statutory period for reply expire later than SIX MONTHS from the mailing date of this final action.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to JOEL G. HORNING whose telephone number is (571) 270-5357. The examiner can normally be reached on M-F 9-5pm with alternating Fridays off.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Michael B. Cleveland can be reached on (571)272-1418. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <http://pair-direct.uspto.gov>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/J. G. H./
Examiner, Art Unit 1792

/Michael Cleveland/
Supervisory Patent Examiner, Art Unit 1792